Three years (2008-2010) measurements of atmospheric concentrations of organochlorine pesticides (OCPs) at Station Nord, North East Greenland

Rossana Bossi,*[a] Carsten Ambelas Skjøth[b] and Henrik Skov[a,c]

[a] Aarhus University, Department of Environmental Science, Frederiksborgvej 399, 4000 Roskilde, Denmark.

[b] University of Worcester, Henwick Grove, Worcester WR2 6AJ, United Kingdom.

[c] University of Southern Denmark, Institute of Chemical Engineering and Biotechnology and Environmental Technology, 5500 Odense, Denmark.

*Corresponding Author, Tel: +45-87158603; E-mail: rbo@dmu.dk

Electronic Supplementary Information

Analytical method

The list of compounds included in the analytical method is shown in Table ESI 1. Before extraction the samples are spiked with 25 ng each of a mix of ^{13}C-labelled compounds (POPs Pesticides HRMS Clean-up spike ^{13}C, Cambridge Isotope Laboratories). The individual surrogate standards are listed in Table ESI 1. The samples are then Soxhlet extracted with 600 ml n-hexane/acetone (4:1, v/v) for 8 hours at 75˚C. All the solvents used are glass distilled grade from Rathburn (Walkerburn, UK). The solvent is evaporated with a rotary evaporator at 30˚C to about 5 ml. The extract is further evaporated to about 1 ml under a gentle stream of nitrogen at 20˚C. A 6 ml glass column packed with 1 g silica (Isolute®SPE, Biotage, Lund, Sweden) is conditioned with 5 ml n-hexane and the sample extract is passes through the column applying light vacuum. The analytes are eluted with 5 ml n-hexane followed by 5 ml n-hexane/dichloromethane (1:1, v/v). The two fractions are combined and evaporated under a gentle stream of nitrogen at 20˚C. The sample is reconstituted in 1ml isooctane spiked with 25 ng $^{13}C_6$-PCB-53 (Cambridge Isotope Laboratories) and analysed by gas chromatography-high resolution mass spectrometry (GC-HRMS).

The gas chromatographic conditions are the following: separation on a 60 m x 0.22 mm, 0.25 µm film thickness DB-5 MS column (Agilent Technologies, Santa Clara, CA, USA); carrier gas, He at a flow of 0.8 ml/min; splitless injection of 1 µl at 200° C; temperature program 100°C for 1 min, then 30°C/min to 190°C, and 2°C/min to 290°C, hold for 5 min. The HRMS (DFS, Thermo Scientific, Bremen, Germany) is set up in the multiple ion detection mode (MID) at a resolution of 10,000 (10% valley definition). FC43 (perfluorotributylamine) is used as a reference compound to provide the inherent lock and calibration masses.

Table ESI 1. MS ions for Selected Ion Monitoring for target analytes and internal standards.

Compound	*Quantifier ion (m/z)*	*Qualifier ion (m/z)*
α-HCH	216.9145	218.9116
β-HCH	216.9145	218.9116
γ-HCH	216.9145	218.9116
δ-HCH	216.9145	218.9116
Hexachlorobenzene	283.8102	285.8072
Heptachlor	271.8096	273.8067
Heptachlor Epoxide	352.8442	354.8413
Aldrin	262.8564	264.8535
Dieldrin	262.8564	264.8535
Endrin	262.8564	264.8535
trans-Chlordane	372.8254	374.8225
cis-Chlordane	372.8254	374.8225
trans-Nonachlor	406.7864	408.7835
cis-Nonachlor	262.8564	264.8535
Endosulfan I	338.8730	340.8700
Endosulfan II	262.8564	264.8535
Endosulfan sulfate	262.8564	264.8535
o,p'-DDE	317.9345	318.9379
p,p'-DDE	245.9998	247.9968
o,p'-DDD	235.0076	237.0046
p,p'-DDD	235.0076	237.0046
o,p'-DDT	235.0076	237.0046
p,p'-DDT	235.0076	237.0046
Endrin ketone	247.8521	249.8921
Methoxychlor	227.1067	228.1100
Surrogate standards		
α-HCH $^{13}C_6$	222.9341	224.9312
β-HCH $^{13}C_6$	222.9341	224.9312
γ-HCH $^{13}C_6$	222.9341	224.9312
δ -HCH $^{13}C_6$	222.9341	224.9312
Hexachlorobenzene $^{13}C_6$	289.8303	291.8273
Aldrin $^{13}C_{12}$	269.8799	271.8769
Dieldrin $^{13}C_{12}$	269.8799	271.8769
Endrin $^{13}C_{12}$	269.8799	271.8769
Heptachlor $^{13}C_{10}$	276.8264	278.8234
Heptachlor epoxide $^{13}C_{10}$	362.8772	364.8743
trans-Chlordane $^{13}C_{10}$	382.8590	384.8560
trans-Nonachlor $^{13}C_{10}$	416.8200	418.8170
cis-Nonachlor $^{13}C_{10}$	269.8799	271.8769
o,p'-DDE $^{13}C_{12}$	327.9777	329.9748
p,p'-DDE $^{13}C_{12}$	245.9998	247.9968
o,p'-DDD $^{13}C_{12}$	247.0481	249.0449
p,p'-DDD $^{13}C_{12}$	247.0481	249.0449
o,p'-DDT $^{13}C_{12}$	247.0481	249.0449
p,p'-DDT $^{13}C_{12}$	247.0481	249.0449
Recovery standard		
PCB-51 $^{13}C_6$	301.9626	303.9597

Table ESI 2. Average recoveries (%) of the labeled surrogate standards (± RSD%) from PUF/XAD and filter samples.

Compound	*Average recoveries PUF/XAD*	*Average recoveries filters*
α-HCH $^{13}C_6$	84 (± 25)	68 (± 20)
β-HCH $^{13}C_6$	63 (± 22)	79 (± 20)
γ-HCH $^{13}C_6$	102 (± 40)	72 (± 20)
δ-HCH $^{13}C_6$	136 (± 20)	79 (± 21)
Hexachlorobenzene $^{13}C_6$	82 (± 17)	90 (± 11)
Aldrin $^{13}C_{12}$	59 (± 10)	69 (±22)
Dieldrin $^{13}C_{12}$	55 (± 18)	70 (± 18)
Endrin $^{13}C_{12}$	78 (± 16)	74 (± 33)
Heptachlor $^{13}C_{10}$	99 (± 13)	78 (± 20)
Heptachlor epoxide $^{13}C_{10}$	63 (± 9)	79 (± 22)
trans-Chlordane $^{13}C_{10}$	54 (± 19)	79 (± 16)
trans-Nonachlor $^{13}C_{10}$	59 (± 11)	76 (±14)
cis-Nonachlor $^{13}C_{10}$	48 (± 20)	69 (± 25)
o,p'-DDE $^{13}C_{12}$	66 (± 16)	83 (± 29)
p,p'-DDE $^{13}C_{12}$	53 (± 11)	81 (± 16)
o,p'-DDD $^{13}C_{12}$	46 (± 16)	66 (±28)
p,p'-DDD $^{13}C_{12}$	45 (± 20)	72 (± 26)
o,p'-DDT $^{13}C_{12}$	68 (± 15)	87 (± 16)
p,p'-DDT $^{13}C_{12}$	97 (± 27)	96 (± 16)

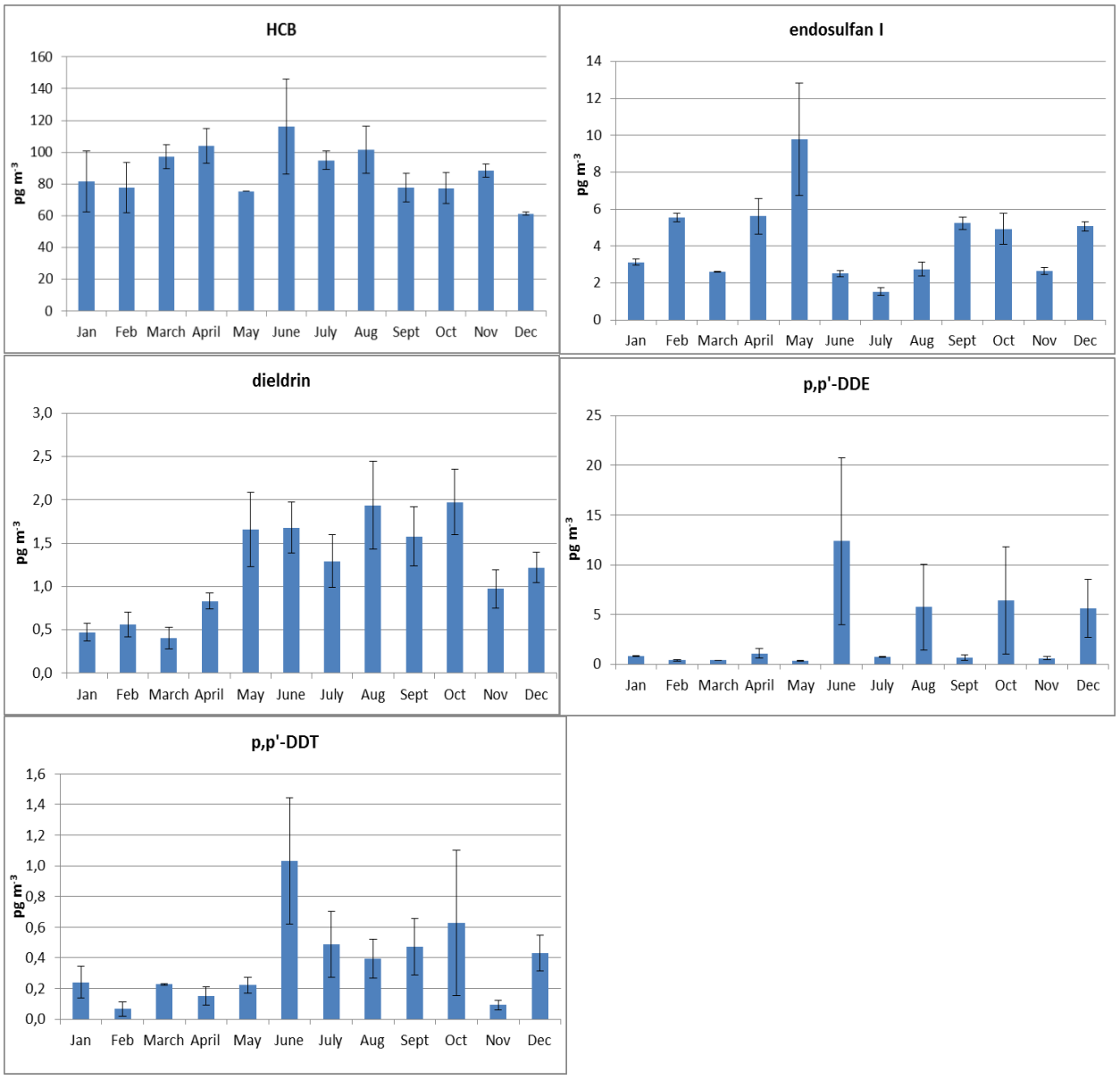

Figure ESI 1. Monthly time series (average of 3 years) of hexachlorobenzene (HCB), endosulfan, dieldrin and DDTs. The error bars indicate ± standard deviation of the measurements.

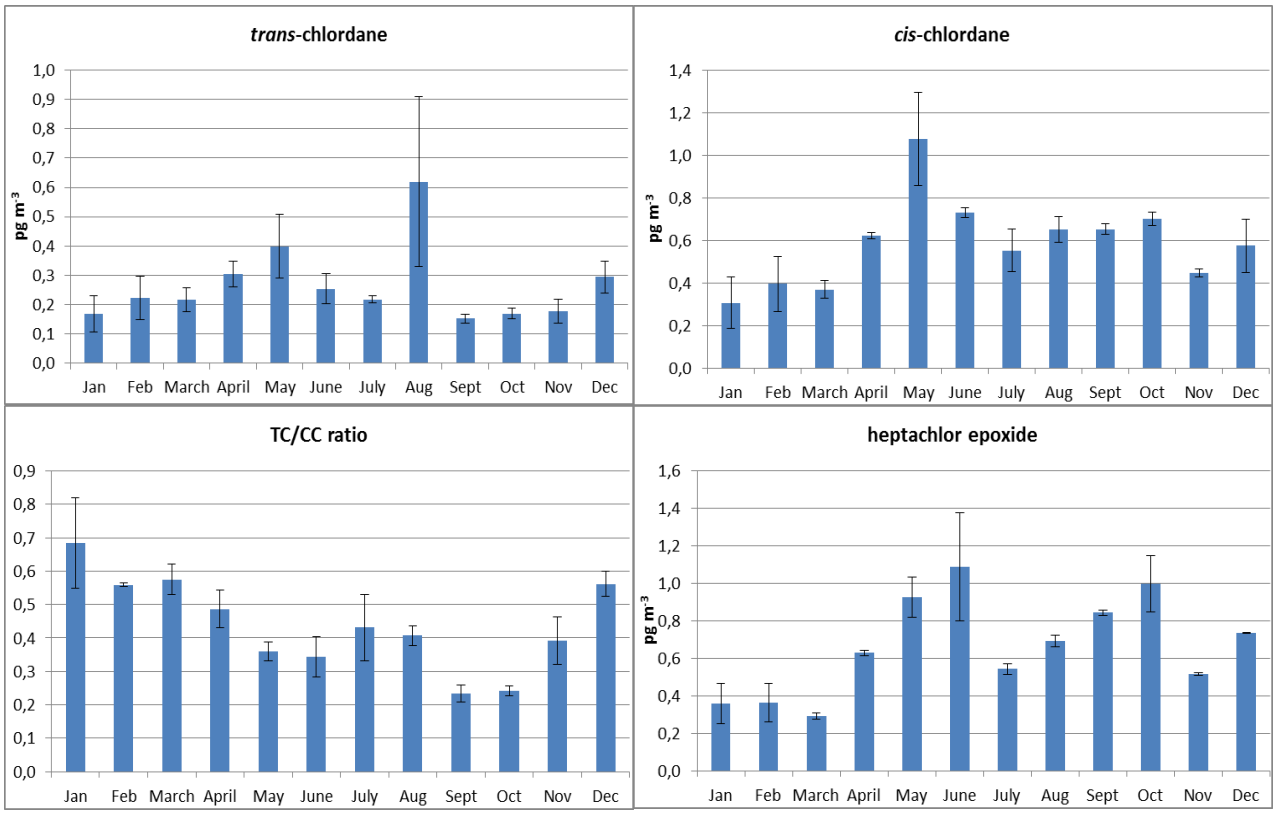

Figure ESI 2. Monthly time series (average of 3 years) of chlordane-related compounds and TC/CC ratio. The error bars indicate ± standard deviation of the measurements.

Table ESI 3. Measured concentrations of selected OCPs in 2008 at Station Nord (pg/m^3); the date given is for the start of the sampling period, which is of 1-week duration.

Compound	14-01-2008	11-02-2008	10-03-2008	31-03-2008	28-04-2008	09-06-2008	07-07-2008	04-08-2008	01-09-2008	29-09-2008	27-10-2008	24-11-2008	22-12-2008
α-HCH	9.9	8.3	5.7	6.2	6.5	9.5	7.4	12.1	16.0	15.0	14.3	9.2	7.3
γ-HCH	1.0	1.3	1.01	0.07	0.6	0.9	0.6	0.5	1.0	0.7	0.3	0.4	1.1
Hexachlorobenzene	108.7	113.9	108.0	119.5	-	158.7	103.0	122.6	74.6	115.4	96.4	94.5	63.0
Heptachlor	0.05	0.07	0.2	0.1	0.1	0.2	0.3	0.09	0.1	0.03	0.02	<0.001	0.06
Heptachlor epoxide	0.5	0.6	0.3	0.6	1.1	0.7	0.6	0.7	0.9	0.8	0.8	0.5	0.7
Dieldrin	0.3	0.8	0.6	1.0	2.3	1.3	0.9	1.2	1.3	1.1	1.8	1.3	1.6
trans-Chlordane	0.2	0.4	0.3	0.4	0.6	0.3	0.2	0.2	0.1	0.1	0.2	0.2	0.4
cis-Chlordane	0.4	0.7	0.4	0.6	1.4	0.8	0.7	0.6	0.7	0.6	0.8	0.5	0.8
trans-Nonachlor	0.3	0.4	0.2	0.4	1.1	0.7	0.4	0.5	0.4	0.4	0.5	0.3	0.4
cis-Nonachlor	0.03	<0.002	<0.002	0.05	0.06	0.1	0.04	0.07	0.07	0.04	0.04	0.04	0.06
Endosulfan I	2.9	5.9	2.7	4.2	14.1	2.7	1.9	2.1	5.0	3.2	5.8	2.9	5.4
o,p'-DDE	0.08	0.08	<0.001	0.1	0.02	<0.001	0.02	<0.001	0.03	<0.001	0.02	0.03	0.06
p,p'-DDE	0.4	0.6	0.4	0.4	0.4	0.5	0.3	0.3	0.3	0.07	0.2	0.5	0.8
o,p'-DDD	<0.001	0.03	0.07	<0.001	0.05	0.1	0.1	0.1	0.1	0.02	0.02	0.06	0.08
p,p'-DDD	0.01	<0.001	0.04	0.02	0.03	0.1	0.1	0.1	0.07	<0.001	<0.001	0.05	0.04
o,p'-DDT	0.1	0.2	0.1	0.2	0.3	0.3	0.1	0.1	0.2	0.1	0.1	0.2	0.3
p,p'-DDT	0.07	0.1	0.2	0.06	0.1	0.4	0.2	0.2	0.3	0.06	0.06	0.1	0.3

Table ESI 4. Measured concentrations of selected OCPs in 2009 at Station Nord (pg/m^3); the date given is for the start of the sampling period, which is of 1-week duration.

Compound	19-01-2009	16-02-2009	24-08-2009	21-09-2009	19-10-2009	23-11-2009	21-12-2009
α-HCH	8.9	4.7	13.6	11.3	8.5	0.9	7.8
γ-HCH	1.0	0.8	11.8	2.2	2.1	0.1	1.4
Hexachlorobenzene	54.6	57.1	-	61.6	57.1	1.8	59.7
Heptachlor	0.006	0.06	0.6	0.04	0.04	0.07	0.02
Heptachlor epoxide	0.5	0.2	0.8	0.9	1.3	0.07	0.7
Dieldrin	0.7	0.3	17.0	2.6	2.8	0.5	1.2
trans-Chlordane	0.3	0.1	1.0	0.2	0.1	0.02	0.2
cis-Chlordane	0.5	0.2	0.8	0.6	0.6	0.01	0.4
trans-Nonachlor	0.5	0.1	0.2	0.02	0.06	0.04	<0.001
cis-Nonachlor	<0.002	0.01	<0.002	0.1	0.02	<0.002	<0.002
Endosulfan I	3.3	0.9	3.6	4.7	3.0	0.3	0.2
o,p'-DDE	<0.001	<0.001	0.01	<0.001	0.02	<0.001	<0.001
p,p'-DDE	0.6	0.3	15.7	1.3	18.8	1.0	10.5
o,p'-DDD	0.02	<0.001	6.2	0.5	0.01	0.07	<0.001
p,p'-DDD	0.03	0.02	6.2	0.7	0.1	0.01	0.06
o,p'-DDT	0.2	0.06	4.0	0.5	0.2	<0.001	0.1
p,p'-DDT	0.2	<0.003	5.8	0.9	1.7	0.02	0.6

Table ESI 5. Measured concentrations of selected OCPs in 2010 at Station Nord (pg/m^3); the date given is for the start of the sampling period, which is of 1-week duration.

Compound	18-01-2010	15-02-2010	15-03-2010	12-04-2010	10-05-2010	07-06-2010	05-07-2010	02-08-2010	30-08-2010	27-09-2010	08-11-2010	06-12-2010
α-HCH	1.1	5.2	9.0	9.7	9.7	6.0	8.0	10.5	14.7	15.1	11.0	0.1
γ-HCH	2.2	0.9	1.1	1.3	0.4	0.3	0.6	0.6	1.1	1.5	1.1	0.5
Hexachlorobenzene	1.8	61.6	86.6	88.7	75.5	73.6	86.6	80.4	97.2	78.9	82.4	1.1
Heptachlor	0.02	0.04	<0.001	<0.001	0.05	<0.001	1.0	1.1	0.2	0.1	0.05	0.008
Heptachlor epoxide	0.1	0.3	0.3	0.7	0.8	1.5	0.5	0.6	0.8	0.9	0.5	0.2
Dieldrin	0.4	0.6	0.2	0.7	1.1	2.1	1.7	2.7	1.3	1.3	0.7	0.9
trans-Chlordane	0.03	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.1	0.1
cis-Chlordane	0.03	0.3	0.3	0.6	0.8	0.7	0.4	0.6	0.7	0.7	0.4	0.2
trans-Nonachlor	0.03	0.1	0.2	0.5	0.7	1.6	0.5	0.5	0.5	0.5	0.3	0.09
cis-Nonachlor	<0.001	0.01	<0.001	0.02	0.1	0.2	0.07	0.09	0.08	0.1	<0.001	<0.001
Endosulfan I	0.1	5.2	2.6	7.0	5.5	2.3	1.2	2.6	6.0	6.0	2.4	4.7
o,p'-DDE	0.03	0.02	0.2	0.06	<0.001	<0.001	0.07	0.1	<0.001	<0.001	<0.001	<0.001
p,p'-DDE	1.5	0.4	0.4	1.8	0.3	24.3	1.2	1.3	0.4	0.2	0.3	0.2
o,p'-DDD	0.06	0.02	0.07	0.03	0.1	0.2	0.4	0.5	0.1	0.06	0.02	0.05
p,p'-DDD	0.1	0.03	0.08	0.07	0.2	0.4	0.6	0.06	0.2	0.06	0.03	0.07
o,p'-DDT	0.06	<0.001	0.3	0.2	0.2	0.2	0.4	0.4	0.2	0.1	0.1	0.1
p,p'-DDT	0.5	<0.003	0.2	0.2	0.3	1.6	0.8	0.6	0.2	0.1	0.1	0.2